

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
4 April 2002 (04.04.2002)

PCT

(10) International Publication Number
WO 02/26628 A1

(51) International Patent Classification⁷: **C01G 11/05**

(21) International Application Number: **PCT/US01/16036**

(22) International Filing Date: **19 May 2001 (19.05.2001)**

(25) Filing Language: **English**

(26) Publication Language: **English**

(30) Priority Data:
09/574,262 **19 May 2000 (19.05.2000)** **US**

(71) Applicant: **EXXONMOBIL CHEMICAL PATENTS INC.** [US/US]; 5200 Bayway Drive, Baytown, TX 77520-5200 (US).

(72) Inventor: **STUNTZ, Gordon, F.**; 12217 Lake Lingham Circle, Baton Rouge, LA 70816 (US).

(74) Agents: **ZBORAY, James, A. et al.**; ExxonMobil Chemical Company, P.O. Box 2149, Baytown, TX 77522-2149 (US).

(81) Designated States (*national*): AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: **PROCESS FOR SELECTIVELY PRODUCING C₃ OLEFINS IN A FLUID CATALYTIC CRACKING PROCESS**

(57) Abstract: A process for producing polymers from olefins selectively produced from a catalytically cracked or thermally cracked naphtha stream is disclosed herein. The naphtha stream is introduced into a process unit comprised of a reaction zone, a stripping zone, a catalyst regeneration zone, and a fractionation zone. The naphtha feedstream is contacted in the reaction zone with a catalyst containing from about 10 to 50 wt.% of a crystalline zeolite having an average pore diameter less than about 0.7 nanometers at reaction conditions which include temperatures ranging from about 500° to 650 °C and a hydrocarbon partial pressure from about 10 to 40 atm. The naphtha products are collected over the catalyst in the reaction zone and sent to the stripping zone. Volatiles are stripped with steam in the stripping zone and the catalyst particles are sent to the catalyst regeneration zone where coke is burned from the catalyst, which is then recycled to the reaction zone. Overhead products from the reaction zone are passed to a fractionation zone where a stream of C₃ products is recovered and a stream rich in C₄ and/or C₅ olefins is recycled to the stripping zone. The olefins can be further processed and polymerized to form a variety of polymer materials.

**PROCESS FOR SELECTIVELY PRODUCING C₃ OLEFINS IN A
FLUID CATALYTIC CRACKING PROCESS**

Cross-Reference To Related Application

5 This is a continuation-in-part of U.S. Patent Application Serial No.
09/073,083, filed May 5, 1998.

Background

10 The present invention relates to a process for producing propylene from a
naphtha stream.

 The need for low emissions fuels has created an increased demand for light
olefins used in alkylation, oligomerization, MTBE and ETBE synthesis processes.
In addition, a low-cost supply of light olefins, particularly propylene, continues to
be in demand to serve as feedstock for polyolefin, particularly polypropylene.

15 Fixed bed processes for light paraffin dehydrogenation have recently
attracted renewed interest for increasing olefin production. However, these types
of processes typically require relatively large capital investments and high
operating costs. It is therefore advantageous to increase olefin yield using
processes, which require relatively small capital investment. It would be
20 particularly advantageous to increase olefin yield in catalytic cracking processes
so that the olefins could be further processed into polymers such as
polypropylene.

 A problem inherent in producing olefins products using FCC units is that
the process depends on a specific catalyst balance to maximize production of light
25 olefins while also achieving high conversion of the 650°F + (~340°C) feed
components. In addition, even if a specific catalyst balance can be maintained to
maximize overall olefin production, olefin selectivity is generally low because of
undesirable side reactions, such as extensive cracking, isomerization,
aromatization and hydrogen transfer reactions. Light saturated gases produced
30 from undesirable side reactions result in increased costs to recover the desirable
light olefins. Therefore, it is desirable to maximize olefin production in a process
that allows a high degree of control over the selectivity of C₃ and C₄ olefins.

Summary Of The Invention

One embodiment of the present invention is a process for producing polypropylene comprising the steps of (a) feeding a naphtha stream comprising from about 10 to 30 wt.% paraffins and between about 15 to 70 wt.% olefins and
5 co-feeding a stream comprising C₄ olefins to a process unit comprising a reaction zone, a stripping zone, a catalyst regeneration zone, and a fractionation zone; (b) contacting the naphtha stream with a fluidized bed of catalyst in the reaction zone to form a cracked product, the catalyst comprising a zeolite having an average pore diameter of less than about 0.7 nm and wherein the reaction zone is operated
10 at a temperature from about 500° to 650°C, a hydrocarbon partial pressure of 10 to 40 psia (about 70- about 280 kPa), a hydrocarbon residence time of 1 to 10 seconds, and a catalyst to feed weight ratio between about 4 and about 10, thereby producing a reaction product wherein no more than about 20 wt. % of paraffins are converted to olefins and wherein propylene comprises at least about 90 mol.%
15 of the total C₃ products; (c) passing the catalyst through said stripping zone; (d) passing the stripped catalyst from the stripping zone to the catalyst regeneration zone where the catalyst is regenerated in the presence of an oxygen-containing gas; (e) recycling the regenerated catalyst to the reaction zone; (f) fractionating the cracked product to produce a C₃ fraction, a C₄ fraction rich in olefins, and
20 optionally a C₅ fraction rich in olefins.

In another embodiment of the present invention the catalyst is a ZSM-5 type catalyst.

In an embodiment of the present invention a C₅ fraction rich in olefins is also recycled.

25 In another embodiment of the present invention the feedstock contains about 10 to 30 wt. % paraffins, and from about 20 to 70 wt. % olefins.

In another embodiment of the present invention the reaction zone is operated at a temperature from about 525°C to about 600°C.

30 Detailed Description Of The Invention

Feedstreams that are suitable for producing the relatively high C₂, C₃, and C₄ olefin yields are those streams boiling in the naphtha range containing from

about 5 wt. % to about 35 wt. %, preferably from about 10 wt. % to about 30 wt. %, and more preferably from about 10 to 25 wt. % paraffins, and from about 15 wt. %, preferably from about 20 wt. % to about 70 wt. % olefins. The feed may also contain naphthenes and aromatics. Naphtha boiling range streams are typically those having a boiling range from about 65°F to about 430°F (about 18°C to about 225°C), preferably from about 65°F to about 300°F (about 18°C to about 150°C).

The naphtha can be a thermally cracked or a catalytically-cracked naphtha. The naphtha streams can be derived from the fluid catalytic cracking (FCC) of gas oils and resids, or they can be derived from delayed or fluid coking of resids. Preferably, the naphtha streams used in the practice of the present invention derive from the fluid catalytic cracking of gas oils and resids. FCC naphthas are typically rich in olefins and/or diolefins and relatively lean in paraffins. It is within the scope of the instant invention to feed or co-feed other olefinic streams that are not catalytically- or thermally-cracked naphthas into said reaction zone with the primary feed. It is believed that this will increase the yield of propylene.

In another embodiment of the present invention, a C₄ olefin stream containing n-butenes is co-fed with the naphtha feed. The C₄ olefin stream may come from suitable sources such as conventional FCC units, coker units, steam crackers and other process units that produce C₄ olefins streams that can be recycled to the cracking unit. In one embodiment, the C₄ olefin stream may be a raffinate from a methyl-tert-butyl-ether (MTBE) process. MTBE units typically feed a mixture of methanol and C₄ olefins. Only the iso-butylene reacts with the methanol to yield MTBE, leaving a significant amount of C₄ olefins, including n-butenes, in the MTBE raffinate.

The C₄ olefin stream preferably comprises at least about 75 wt.% n-butenes, more preferably greater than about 90 wt.% n-butenes. Streams containing lower amounts of n-butenes are also acceptable, such as where a stream containing a significant amount of diolefins, such as butadiene, is employed. When the C₄ olefin stream is injected into the reaction zone along with the naphtha feed, the C₄ olefins undergo rapid disproportionation reactions with

other olefins in the naphtha feed, followed by cracking reactions. These reactions increase propylene yields.

5 The process of the present invention is performed in a process unit comprising a reaction zone, a stripping zone, a catalyst regeneration zone, and a fractionation zone. The naphtha feed is fed into the reaction zone where it contacts a source of hot, regenerated catalyst. The hot catalyst vaporizes and cracks the feed at a temperature from about 500°C to about 650°C, preferably from about 525°C to about 600°C. The cracking reaction deposits coke on the catalyst, thereby deactivating the catalyst. The cracked products are separated from the coked catalyst and sent to a fractionator. The coked catalyst passes through the stripping zone where a stripping medium, such as steam, strips volatiles from the catalyst particles. The stripping can be preformed under low-severity conditions to retain a greater fraction of adsorbed hydrocarbons for heat balance. The stripped catalyst is then passed to the regeneration zone where it is regenerated by burning coke on the catalyst in the presence of an oxygen containing gas, preferably air. Decoking restores catalyst activity and simultaneously heats the catalyst to a temperature from about 650°C to about 750°C. The hot regenerated catalyst is then recycled to the reaction zone to react with fresh naphtha feed. Flue gas formed by burning coke in the regenerator may be treated for removal of particulates and for conversion of carbon monoxide. The cracked products from the reaction zone are sent to a fractionation zone where various products are recovered, particularly a C₃ fraction, a C₄ fraction, and optionally a C₅ fraction. The C₄ fraction and the C₅ fraction will typically be rich in olefins. One or both of these fractions can be recycled to the reactor. They can be recycled to either the main section of the reactor, or a riser section, or a stripping section. It is preferred that they be recycled to the upper part of the stripping section, or stripping zone. Recycling one or both of these fractions will convert at least a portion of these olefins to propylene.

30 It may also be desirable to inject a C₄ olefin stream into the stripper section. Such a C₄ olefin stream (not to be confused with a C₄ fraction recycled from the cracked products of the cracking process) would be derived from one or more suitable sources such as conventional FCC units, coker units, steam crackers

and other process units that produce C₄ olefins streams that can be recycled to the cracking unit. In one embodiment, the C₄ olefin stream may be a raffinate from a methyl-tert-butyl-ether (MTBE) process as previously described. In another embodiment, the C₄ olefin stream injected into the stripper section also preferably
5 comprises at least about 75 wt.% n-butenes, more preferably greater than about 90 wt.% n-butenes. Streams containing lower amounts of n-butenes are also acceptable, such as where a stream containing a significant amount of diolefins, such as butadiene, is employed.

While attempts have been made to increase light olefins yields in the FCC
10 process unit itself, the present invention uses its own distinct process unit, as previously described, which receives naphtha from a suitable source in the refinery. The reaction zone is operated at process conditions that will maximize C₂ to C₄ olefins (particularly propylene) selectivity with relatively high conversion of C₅+ olefins. Suitable catalysts used with the present invention contain a
15 crystalline zeolite having an average pore diameter less than about 0.7 nanometers (nm), said crystalline zeolite comprising from about 10 wt. % to about 50 wt. % of the total fluidized catalyst composition. It is preferred that the crystalline zeolite be selected from the family of medium-pore size (< 0.7 nm) crystalline aluminosilicates, otherwise referred to as zeolites. Of particular interest are the
20 medium-pore zeolites with a silica to alumina molar ratio of less than about 75:1, preferably less than about 50:1, and more preferably less than about 40:1, although some embodiments may incorporate a silica to alumina ratio greater than 40:1. The pore diameter, also referred to as effective pore diameter, is measured using standard adsorption techniques and hydrocarbonaceous compounds of
25 known minimum kinetic diameters. See Breck, *Zeolite Molecular Sieves*, 1974 and Anderson et al., *J. Catalysis* 58, 114 (1979), both of which are incorporated herein by reference.

Medium-pore size zeolites that can be used in the practice of the present invention are described in "Atlas of Zeolite Structure Types", eds. W. H. Meier
30 and D. H. Olson, Butterworth-Heinemann, Third Edition, 1992, which is hereby incorporated by reference. The medium-pore size zeolites generally have a pore size from about 5 Å to about 7 Å and include for example, MFI, MFS, MEL,

MTW, EUO, MTT, HEU, FER, and TON structure type zeolites (IUPAC Commission of Zeolite Nomenclature). Non-limiting examples of such medium-pore size zeolites, include ZSM-5, ZSM-12, ZSM-22, ZSM-23, ZSM-34, ZSM-35, ZSM-38, ZSM-48, ZSM-50, silicalite, and silicalite 2. The most preferred is ZSM-5, which is described in U.S. Patent Nos. 3,702,886 and 3,770,614. ZSM-11 is described in U.S. Patent No. 3,709,979; ZSM-12 in U.S. Patent No. 3,832,449; ZSM-21 and ZSM-38 in U.S. Patent No. 3,948,758; ZSM-23 in U.S. Patent No. 4,076,842; and ZSM-35 in U.S. Patent No. 4,016,245. All of the above patents are incorporated herein by reference. Other suitable medium-pore size zeolites include the silicoaluminophosphates (SAPO), such as SAPO-4 and SAPO-11 which is described in U.S. Patent No. 4,440,871; chromosilicates; gallium silicates; iron silicates; aluminum phosphates (ALPO), such as ALPO-11 described in U.S. Patent No. 4,310,440; titanium aluminosilicates (TASO), such as TASO-45 described in EP-A No. 229,295; boron silicates, described in U.S. Patent No. 4,254,297; titanium aluminophosphates (TAPO), such as TAPO-11 described in U.S. Patent No. 4,500,651; and iron aluminosilicates.

The medium-pore-size zeolites can include "crystalline admixtures" which are thought to be the result of faults occurring within the crystal or crystalline area during the synthesis of the zeolites. Examples of crystalline admixtures of ZSM-5 and ZSM-11 are disclosed in U.S. Patent No. 4,229,424, which is incorporated herein by reference. The crystalline admixtures are themselves medium-pore-size zeolites and are not to be confused with physical admixtures of zeolites in which distinct crystals of crystallites of different zeolites are physically present in the same catalyst composite or hydrothermal reaction mixtures.

The catalysts of the present invention may be held together with an inorganic oxide matrix material component. The inorganic oxide matrix component binds the catalyst components together so that the catalyst product is hard enough to survive interparticle and reactor wall collisions. The inorganic oxide matrix can be made from an inorganic oxide sol or gel which is dried to "bind" the catalyst components together. Preferably, the inorganic oxide matrix is not catalytically active and will be comprised of oxides of silicon and aluminum. It is also preferred that separate alumina phases be incorporated into the inorganic oxide matrix. Species of

aluminum oxyhydroxides-g-alumina, boehmite, diaspora, and transitional aluminas such as a-alumina, b-alumina, g-alumina, d-alumina, e-alumina, k-alumina, and r-alumina can be employed. Preferably, the alumina species is an aluminum trihydroxide such as gibbsite, bayerite, nordstrandite, or doyleite. The matrix material may also contain phosphorous or aluminum phosphate.

Process conditions include temperatures from about 500°C to about 650°C, preferably from about 500°C to 600°C; hydrocarbon partial pressures from about 10 to 40 psia (about 70-about 280 kPa) to about, preferably from about 20 to 35 psia (about 140- about 245 kPa); and a catalyst to naphtha (wt/wt) ratio from about 3 to 12, preferably from about 4 to 10, where catalyst weight is total weight of the catalyst composite. Steam may be concurrently introduced with the naphtha stream into the reaction zone, with the steam comprising up to about 50 wt. % of the naphtha feed. Preferably, the naphtha residence time in the reaction zone is less than about 10 seconds, for example from about 1 to 10 seconds. The reaction conditions will be such that at least about 60 wt. % of the C₅+ olefins in the naphtha stream are converted to C₄- products and less than about 25 wt. %, preferably less than about 20 wt. % of the paraffins are converted to C₄- products, and that propylene comprises at least about 90 mol.%, preferably greater than about 95 mol. % of the total C₃ reaction products with the weight ratio of propylene/total C₂- products greater than about 3.5.

Preferably, ethylene comprises at least about 90 mol.% of the C₂ products, with the weight ratio of propylene:ethylene being greater than about 4, and that the "full range" C₅+ naphtha product is enhanced in both motor and research octanes relative to the naphtha feed. It is within the scope of this invention to pre-coke the catalysts before introducing the feed to further improve the selectivity to propylene. It is also within the scope of this invention to feed an effective amount of single-ring aromatics to the reaction zone to also improve the selectivity of propylene versus ethylene. The aromatics may be from an external source such as a reforming process unit or they may consist of heavy naphtha recycle product from the instant process.

The following examples are presented for illustrative purposes only and are not to be taken as limiting the present invention in any way.

Examples 1-12

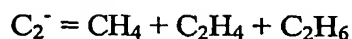
The following examples illustrate the criticality of process operating conditions for maintaining chemical grade propylene purity with samples of cat naphtha cracked over ZCAT-40 (a catalyst that contains ZSM-5) which had been steamed at 1500°F (~815°C) for 16 hrs to simulate commercial equilibrium. Comparison of Examples 1 and 2 show that increasing Cat/Oil ratio improves propylene yield, but sacrifices propylene purity. Comparison of Examples 3 and 4 and 5 and 6 shows reducing oil partial pressure greatly improves propylene purity without compromising propylene yield. Comparison of Examples 7 and 8 and 9 and 10 shows increasing temperature improves both propylene yield and purity. Comparison of Examples 11 and 12 shows decreasing cat residence time improves propylene yield and purity. Example 13 shows an example where both high propylene yield and purity are obtained at a reactor temperature and cat/oil ratio that can be achieved using a conventional FCC reactor/regenerator design for the second stage.

TABLE 1

Example	Feed Olefins, wt%	Temp. —C	Cat/Oil	Oil psia	Oil Res. Time, sec	Cat Res. Time, sec	Wt. %		Propylene Purity, %
							C ₃ ⁺	C ₃ ⁻	
1	38.6	566	4.2	36	0.5	4.3	11.4	0.5	95.8%
2	38.6	569	8.4	32	0.6	4.7	12.8	0.8	94.1%
3	22.2	510	8.8	18	1.2	8.6	8.2	1.1	88.2%
4	22.2	511	9.3	38	1.2	5.6	6.3	1.9	76.8%
5	38.6	632	16.6	20	1.7	9.8	16.7	1.0	94.4%
6	38.6	630	16.6	13	1.3	7.5	16.8	0.6	96.6%
7	22.2	571	5.3	27	0.4	0.3	6.0	0.2	96.8%
8	22.2	586	5.1	27	0.3	0.3	7.3	0.2	97.3%
9	22.2	511	9.3	38	1.2	5.6	6.3	1.9	76.8%
10	22.2	607	9.2	37	1.2	6.0	10.4	2.2	82.5%
11	22.2	576	18.0	32	1.0	9.0	9.6	4.0	70.6%
12	22.2	574	18.3	32	1.0	2.4	10.1	1.9	84.2%
13	38.6	606	8.5	22	1.0	7.4	15.0	0.7	95.5%

Table 1 Continued

<u>Example</u>	<u>Wt.% C₂[≡]</u>	<u>Wt.% C₂[≡]</u>	<u>Ratio of C₃[≡] to C₂[≡]</u>	<u>Ratio of C₃[≡] to C₂[≡]</u>	<u>Wt.% C₃[≡]</u>
1	2.35	2.73	4.9	4.2	11.4
2	3.02	3.58	4.2	3.6	12.8
3	2.32	2.53	3.5	3.2	8.2
4	2.16	2.46	2.9	2.6	6.3
5	6.97	9.95	2.4	1.7	16.7
6	6.21	8.71	2.7	1.9	16.8
7	1.03	1.64	5.8	3.7	6.0
8	1.48	2.02	4.9	3.6	7.3
9	2.16	2.46	2.9	2.6	6.3
10	5.21	6.74	2.0	1.5	10.4
11	4.99	6.67	1.9	1.4	9.6
12	4.43	6.27	2.3	1.6	10.1
13	4.45	5.76	3.3	2.6	15.0



5 The above examples (1,2,7 and 8) show that $C_3^{\equiv}/C_2^{\equiv} > 4$ and $C_3^{\equiv}/C_2^{\equiv} > 3.5$ can be achieved by selection of suitable reactor conditions.

Examples 14 - 17

10 The cracking of olefins and paraffins contained in naphtha streams (e.g. FCC naphtha, coker naphtha) over small or medium-pore zeolites such as ZSM-5 can produce significant amounts of ethylene and propylene. The selectivity to ethylene or propylene and selectivity of propylene to propane varies as a function of catalyst and process operating conditions. It has been found that propylene yield can be increased by co-feeding steam along with cat naphtha to the reactor.

15 The catalyst may be ZSM-5 or other small or medium-pore zeolites. Table 2 below illustrates the increase in propylene yield when 5 wt. % steam is co-fed with an FCC naphtha containing 38.8 wt. % olefins. Although propylene yield increased, the propylene purity is diminished. Thus, other operating conditions may need to be adjusted to maintain the targeted propylene selectivity.

TABLE 2

Example	Steam Co-feed	Temp. C.	Cat/Oil	Oil psia	Oil Res. Time, sec	Cat Res. Time, sec	Wt% Propylene	Wt% Propane	Propylene Purity, %
14	No	630	8.7	18	0.8	8.0	11.7	0.3	97.5%
15	Yes	631	8.8	22	1.2	6.0	13.9	0.6	95.9%
16	No	631	8.7	18	0.8	7.8	13.6	0.4	97.1%
17	Yes	632	8.4	22	1.1	6.1	14.6	0.8	94.8%

Examples 18 - 21

ZCAT-40 was used to crack cat cracker naphtha as described for the above examples. The coked catalyst was then used to crack a C₄ stream composed of 6 wt.% n-butane, 9 wt.% i-butane, 47 wt.% 1-butene, and 38 wt.% i-butene in a reactor at the temperatures and space velocities indicated in the table below. As can be seen from the results in the table below, a significant fraction of the feed stream was converted to propylene.

TABLE 3

10	WHSV, Hr-1	35	18	12	6
	Temperature °C	575	575	575	575
	Butylene Conversion wt. %				
	<u>Product Yields, wt. %</u>				
15	Ethylene	2.4	4.7	5.9	8.8
	Propylene	20.5	27.1	28.8	27.4
	Butylenes	39.7	29.0	25.5	19.2
	C ₁ -C ₄ Light Saturates	18.2	19.2	19.8	22.0
20	C ₅ + Products	19.3	20.0	20.0	22.6

Light olefins resulting from the preferred process may be used as feeds for processes such as oligimerization, polymerization, co-polymerization, ter-polymerization, and related processes (hereinafter "polymerization") to form macromolecules. Such light olefins may be polymerized both alone and in combination with other species, in accordance with polymerization methods known in the art. In some cases it may be desirable to separate, concentrate, purify, upgrade, or otherwise process the light olefins prior to polymerization. Propylene and ethylene are preferred polymerization feeds. Polypropylene and polyethylene are preferred polymerization products made therefrom.

CLAIMS:

1. A process for producing propylene comprising the steps of:
- 5 (a) feeding a naphtha stream comprising from 10 to 30 wt.% paraffins and between 15 to 70 wt.% olefins to a process unit comprising a reaction zone, a stripping zone, a catalyst regeneration zone, and a fractionation zone;
- 10 (b) feeding a stream comprising C₄ olefins to said process unit;
- (c) contacting the naphtha stream with a fluidized bed of catalyst in the reaction zone to form a cracked product, the catalyst comprising a zeolite having an average pore diameter of less than 0.7 nm and wherein the reaction zone is operated at a temperature from 500° to 650°C, a hydrocarbon partial pressure of 10 to 40 psia, a hydrocarbon residence time of 1 to 10 seconds, and a catalyst to feed weight ratio between 4 and 10, thereby producing a reaction product wherein no more than 20 wt. % of paraffins are converted to olefins and wherein propylene comprises at least 90 mol.% of the total C₃ products;
- 15 (d) passing the catalyst through said stripping zone;
- 20 (e) passing the stripped catalyst from the stripping zone to the catalyst regeneration zone where the catalyst is regenerated in the presence of an oxygen-containing gas;
- (f) recycling the regenerated catalyst to the reaction zone;
- 25 (g) fractionating the cracked product to produce a C₃ fraction, a C₄ fraction rich in olefins, and optionally a C₅ fraction rich in olefins;
- (h) recycling the C₄ fraction rich in olefins to the reaction zone, stripping zone, or both.
- 30 2. The process of claim 1 wherein the C₄ olefin stream is fed into the reaction zone.

3 The process of claim 2 wherein the C₄ olefin stream is also fed into
the stripping zone.

5 4. The process of claim 1 wherein the C₄ olefin stream is fed into the
stripping zone.

5. The process of claim 1 wherein the C₄ olefin stream is derived
from a MTBE unit, an FCC unit, a stream cracker, or a coker unit.

10 6. The process of claim 1 wherein the C₄ olefin stream is an MTBE
raffinate stream.

7. The process of claim 1 wherein the C₄ olefin stream is passed to
the process unit from a steam cracker.

15

8. The process of claim 1 wherein the C₄ olefin stream comprises at
least 75 wt.% n-butenes.

20 9. The process of claim 1 wherein the crystalline zeolite is selected
from the ZSM series.

10. The process of claim 9 wherein the crystalline zeolite is ZSM-5.

25 11. The process of claim 10 wherein the reaction temperature is from
500°C to 600°C.

12. The process of claim 10 wherein at least 60 wt. % of the C₅⁺ olefins
in the feedstream is converted to C₄- products and less than 25 wt. % of the
paraffins are converted to C₄- products.

30

13. The process of claim 12 wherein propylene comprises at least 95
mol. % of the total C₃ products.

14. The process of claim 13 wherein the weight ratio of propylene to total C₂- products is greater than 3.5.

5 15. The process of claim 1 further comprising the step of producing said C₅ fraction and recycling said C₅ fraction to the reaction zone, the stripping zone, or both.

10 16. The process of claim 1 further comprising the step of separating propylene from the C₃ fraction and polymerizing the propylene to form polypropylene.

INTERNATIONAL SEARCH REPORT

Internat: Application No

PCT/US 01/16036

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C10G11/05

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
L, X	WO 99 57225 A (EXXON RESEARCH ENGINEERING CO) 11 November 1999 (1999-11-11) * L: priority * claims 1-9 page 5, line 1 - line 5 -----	1-16



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

1 August 2001

Date of mailing of the international search report

21/08/2001

European Patent Office
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Zuurdeeg, B

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internat. Application No

PCT/US 01/16036

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9957225 A	11-11-1999	US 6093867 A	25-07-2000
		AU 3667099 A	23-11-1999
		BR 9910216 A	09-01-2001
		CN 1299402 T	13-06-2001
		EP 1112336 A	04-07-2001

Form PCT/ISA/210 (patent family annex) (July 1992)